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14. ABSTRACT

Vanadium dioxide undergoes a first-order transition from a high-temperature metallic phase to a low-temperature insulating phase at almost the room temperature (T=340K). VO2 has attracted a great deal of attention for its ultrafast optical response whose origin is still mysterious. From the perspective of applications, to control the properties of Vanadium Oxide for device applications, it is essential to understand the effects of compressive and tensile stress resulting from the various substrates, on which the films are deposited. We have examine microscopically the influence of strain on the electronic structure of VO2. We carried out the many body calculation for the low energy model of unstrained VO2 using a new LDA+DMFT methodology that fits existing photoemission and X-ray absortion experiments. We established that factors other than the Peierls distortion play a defining role in driving the MIT in VO2. Strain, besides modifying the bonding antibonding splitting of the a_1g orbitals, increases the band-width and decreases the strength of the correlations. Furthermore, strain shifts the edge of the eg_pi orbital, decreasing the indirect orbital gap. This new insight suggest new avenues for optimizing the properties VO2 via different substitutions. Theoretical predictions for

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Final Report on DARPA grant W911NF-08-1-0203: A Theoretical Exploration of the Metal Insulator Transition in Vanadium Dioxide with an Eye Towards Applications: a First Principles Approach

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1 Executive Summary

Vanadium oxides are very interesting compounds which exhibit exotic transport phenomena. In particular vanadium dioxide (VO_2) undergoes a first-order transition from a high-temperature metallic phase to a low-temperature insulating phase at almost the room temperature ($T = 340\,\mathrm{K}$) [1]. The resistivity jumps by several orders of magnitude through this transition, and the crystal structure changes from rutile (R-phase) at high-temperature to monoclinic (so-called M1-phase) at low-temperature [1, 2]. The latter is characterized by a dimerization of the vanadium atoms into pairs, as well as a tilting of these pairs with respect to the c-axis [3, 4]. VO_2 has also attracted a great deal of attention for its ultrafast optical response, switching between the R and the M1 phase [5, 6, 7]. Despite the large number of experimental [7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18] and theoretical [19, 20, 21, 22, 23, 24, 25] studies focusing on this material the physics driving this phase transition and the resulting optical properties is still mysterious. There are intensive efforts around the world to make devices such as switches, transistors, detectors, varistors, phase change memory, exploiting the unique properties of VO_2.

Two physical effects, Peierls[26], i.e. dimerization, and the Mott mechanism[27] due to strong Coulomb repulsion are important in the metal-insulator transition (MIT) of VO_2. Understanding the detailed interplay and the relative importance of both Peierls and Mott mechanism is important for controlling this material with an eye towards applications. For example, whether the driving force of this transition is electronic (i.e. occurring on femtosecond timescales) or structural (occurring on the picosecond timescale) is important to understand the speed of the switching from the M1 to the rutile phase. From the perspective of appli-
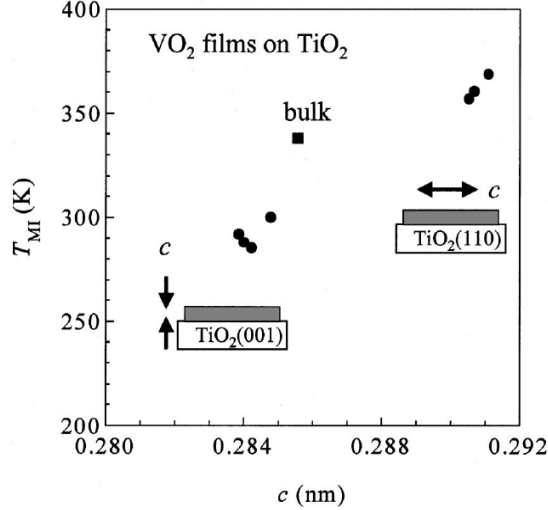
Figure 1: Measurements of VO$_2$ tin films on TiO2 substrate show the unexpected result: Compression of the rutile c-axis (achieved on TiO$_2$ (001) substrate) leads to destabilization of insulator, hence T$_c$ decreases. The expansion of the rutile c-axis leads to higher T$_c$. From [8].

cations, to control the properties of vanadium dioxide for device applications, it is essential to understand the effects of compressive and tensile stress resulting from the various substrates, on which the films are deposited [8, 9].

The experimental results of Ref. [8] showed that compressive uniaxial strain (along the rutile c-axis) stabilizes the metallic phase. These results are reproduced in Fig. 1. They cannot be explained in a simple Peierls picture, which predicts that a compression along the rutile c-axis increases the bonding antibonding splitting. The Pierls mechanism thus increases the tendency to open the gap in the M1 phase, which stabilizes the insulating phase at the expense of the metallic phase. In this picture, the transition temperature would increase under uniaxial compressive strain, opposite to measurements displayed in Fig. 1.

We have examined microscopically the influence of strain on the electronic structure of VO$_2$. We carried out the many-body calculation for the low energy model of unstrained VO$_2$ using a new LDA+DMFT methodology [28] that fits existing photoemission and X-ray absorption experiments better than previous work [19]. We carried out the first LDA+DMFT calculations of VO$_2$ under strain. We established that factors other than the Peierls distortion play a defining role in driving the MIT in VO$_2$. Strain, besides modifying the bonding antibonding splitting of the a_{1g} orbitals, increases the band-width and decreases the strength of the correlations. Furthermore, strain shifts the edge of the e_g^π orbital, decreasing the indirect orbital gap. This new insight suggests new avenues for optimizing the properties VO$_2$ via different substitutions. Theoretical predictions for the strain dependence of many spectroscopic quantities are obtained,

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including the photoemission, the optical conductivity, the inverse photoemission and XAS and ARPES in the M1 and rutile phase. The strain dependence of the ARPES results for the M1 phase give interesting clues to the anisotropy observed in the transport in the counterpart experimental study. The insights obtained in this study together with the computational machinery developed, will serve as a basis for rational material design of VO_2 based applications.

(1) **Downfolded Parametrization:** as a first step we determined a downfolded parametrization of the low energy Hamiltonian including all the t_{2g} orbitals. We determined the strength of interaction, which best fits the low energy properties of this material, such as the optical gap in the M1 phase and the plasma frequency in the rutile phase. It requires a value of $U = 2.2\,\text{eV}$, which is more screened than the values considered in the literature so far [19].

(2) **Orbitally resolved many body spectra:** We carried out first principles LDA+DMFT calculations and obtained orbitally resolved spectral functions, which can be measured in angle integrated photoemission and XAS. Our theoretical results compared very well with existing experiments in the literature.

(3) **Effects of strain:** We carried out LDA+DMFT studies of the modifications that take place in the spectral functions as a result of application of strain.

(4) **Optics:** We carried out LDA+DMFT optical conductivity studies. In the unstrained compound the theoretical results are in good agreement with experiments if we take into account the limitations of the downfolded model. We predicted the evolution of the optical conductivity with strain.

(5) **ARPES:** We carried out studies of ARPES in the M1 phase to understand the possible anisotropy of the transport properties.

(6) **Role of oxygen:** We began explorations of the role of the oxygens in this compound going beyond the downfolded model. Preliminary results in this direction suggest that the oxygen degrees of freedom play a very important role, and their explicit inclusion (rather than their implicit inclusion via downfolding) will result in even more accurate descriptions of the physical properties of this material at all energy scales.

2 Progress Statement

2.1 Downfolded Parametrization

Using LDA we determined the evolution of all hopping parameters of the low energy downfolded Hamiltonian (includes all three t_{2g} orbitals) as a function of strain. Fig. 2 illustrates the strained applied in the calculations in both the
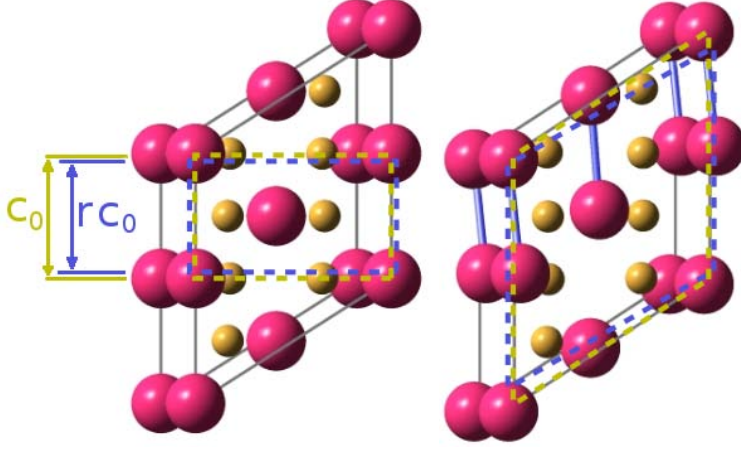
Figure 2: Left: The high temperature metallic rutile structure. Right: The low temperature insulation M1 structure. The yellow box shows the unit cell, and the blue box shows the stressed unit cell. The height of the unstressed (stressed) rutile unit cell is c_0 ($c = rc_0$). The stress preserves the volume of the unit cell, while it expands (compresses) the rutile c axis and compresses (expands) the rutile a axis. The actual stress in theory and experiments is 5×times smaller than shown in the figure.

rutile and M1 phase. The changes of the hopping matrix elements induced by the strain are shown in Fig. 3. While the relative changes in the parameters are small, the manifestations of these changes in the low energy spectral function, and therefore in the transport properties, are very significant.

Fig. 4 shows the LDA partial density of states (DOS) of the low energy t_{2g} sector versus strain. Clearly, the $x^2 - y^2$ (or a_{1g}) orbital, is most effected by strain. The bonding-antibonding splitting increases with compressive strain, while the value of the DOS at the Fermi level remains almost unchanged within LDA.

2.2 LDA+DMFT computations of spectra and validation against existing experiments.

We carried out the first principles LDA+DMFT calculations of *orbitally resolved* spectral functions, which can be measured in angle integrated photoemission and XAS.

There are a large number of experimental studies which have appeared in the last three years. They probe the many body character of the occupied and the unoccupied states in this material and serve as a stringent test of the theoretical approach. This validation is crucial before proceeding to the study of strained materials for which spectroscopic information is not available.
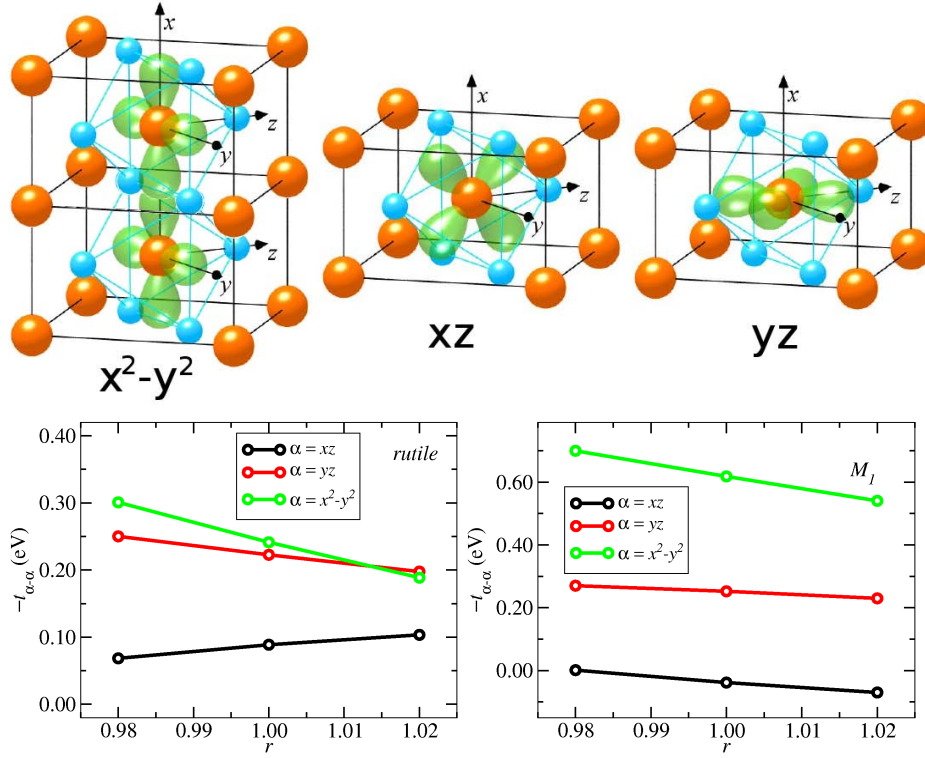
Figure 3: Upper row: The low energy t_{2g} orbitals of VO$_2$. Lower row: The direct V-V hoppings of the low energy Hamiltonian versus strain. The left (right) panel shows the parameters in the rutile (M1) phase. The direction of strain is depicted in Fig. 2.

The results for the orbitally resolved $3d - t_{2g}$ spectral functions of VO$_2$ are shown in Fig. 5. The upfolded density of states of the LDA+DMFT, which includes oxygen $2p$ and the V-$3d - e_g$ states (missing in the downfolded Hamiltonian) are shown in Fig. 6.

In case of the M_1 phase, one can immediately observe from Fig. 5, that only a single state, namely the bonding a_{1g} orbital is occupied. The first two adjacent peaks above the chemical potential are attributed to the e_g^π states, and the third one is due to the a_{1g} state. This is consistent with the recent results of polarization dependent O K x-ray absorption spectroscopy (XAS) experiments from Koethe *at al.* [18]. In this experiment, the orbital character can be determined by changing the polarization of the x-ray from parallel (O K XAS ||) to rutile c-axis to perpendicular polarization (O K XAS $\perp$). The calculated separation between the bonding and anti-bonding peaks of the a_{1g} state is ~ 2.2 eV, which agrees well with the experimentally found value ($2.5 - 2.8$ eV)[18]. The anti-bonding peak is around 1.1 eV above the Fermi level, and
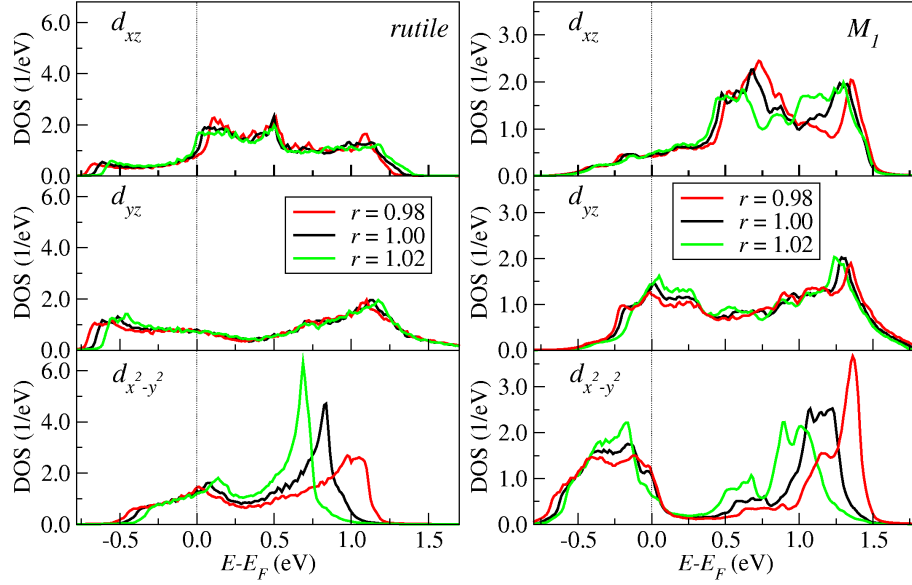
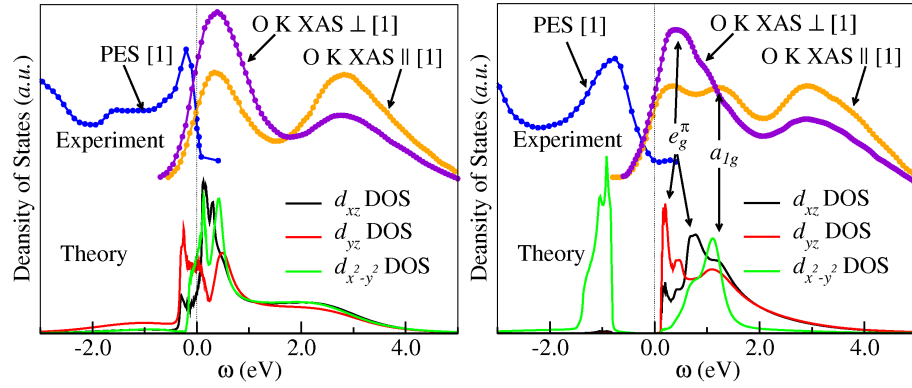Figure 4: Effects of strain (r= c/c_0) on the LDA t_{2g} partial density of states.

Figure 5: The low energy orbitally resolved LDA+DMFT results compared with experiments.

is around ∼ 0.9 eV above the edge of the conduction band. The latter is derived primarily from the e_g^π orbital, as shown in Fig. 5. Finally, we assign the peak around 3 eV to contribution from the e_g states, included in Fig. 6, but excluded in Fig. 5. This is consistent with the experimental finding of Ref. [18] where negligible changes of the peak weight was observed across the MIT, but strong sensitivity to the polarization was noticed.
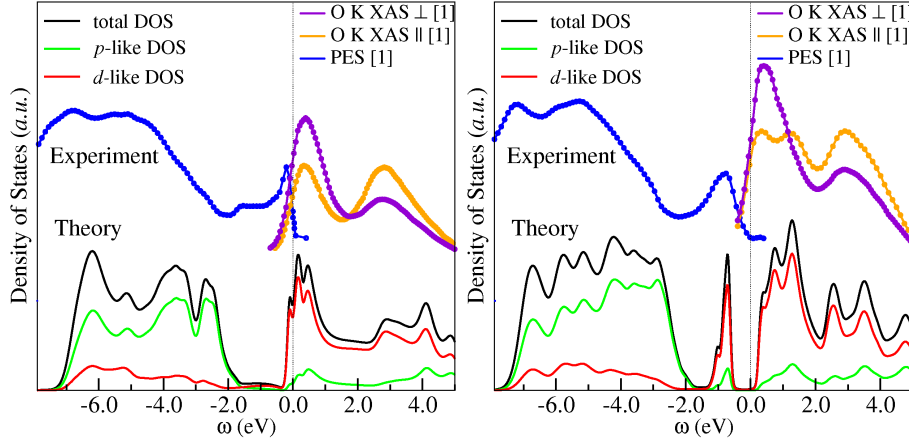
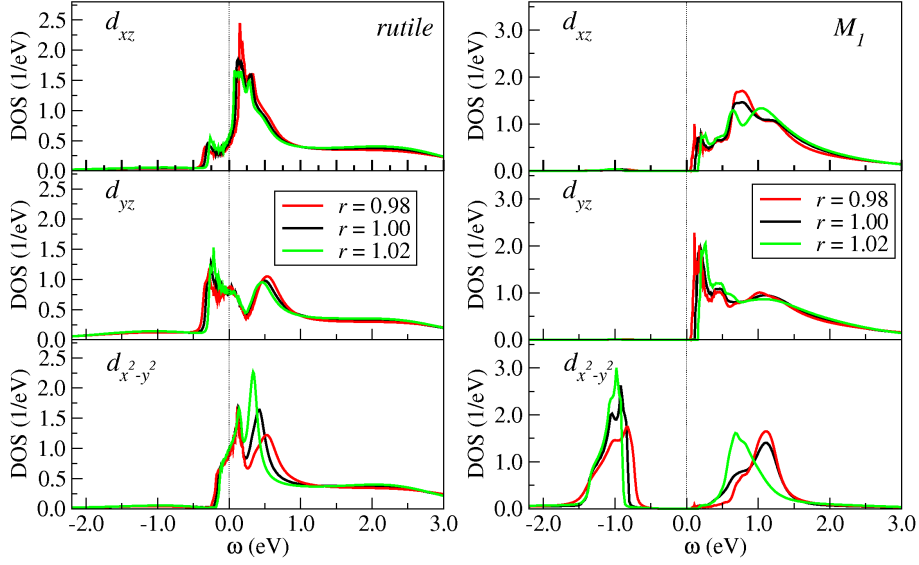Figure 6: Comparison of V-3d, O-2p and the total DOS of LDA+DMFT calculation with experiment.

Figure 7: Effects of strain on the orbitally resolved partial density of states. Left panels correspond to high-temperature rutile phase, and right to low temperature M1-phase.

2.3 Effects of Strain

The effects of applying the uniaxial strain, which corresponds to the effect of substrate stress measured by Muraoka *et. al.* [8], is shown in Fig. 7. First, the rutile phase is very weakly affected by the strain. Two important changes occur
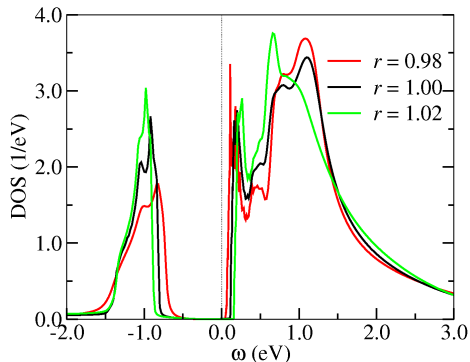
Figure 8: Effects of strain on the total t_{2g} density of states. Compressive strain along the c-axis clearly decreases the gap size and destabilizes the insulating phase, hence decreasing the critical temperature.

in the M1 phase: i) the position and width of the lowest $x^2 - y^2$ peak in the occupied part of the spectrum. The width is increases due to increase of hopping through that orbital (see Fig. 3). The center of this valence band is moved up in energy. ii) Due to decreasing length of the c-axis, the e_g^π states are shifted slightly down towards the Fermi energy. These two effects together result in a substantial contraction of the the gap, as shown in Fig. 8. The decrease of the gap clearly leads to destabilization of the insulating phase and lower transition temperature, as measured by [8].

The gap in the M1 phase clearly decreases with compressive strain. This is in contrast with the expectations from a Pierels picture where the insulating gap is dominate by the bonding-antibonding splitting of the a_{1g} orbitals. While this effect is present in the calculations there is a another physical effect that acts in the opposite direction and turns out to be dominant in VO_2. This is the band broadening effect, due to the increase in the overlap of the orbitals. This effect decreases the strength of correlations and decreasing the size of the gap.

A second effect which cooperates with the enhanced bandwidth and contributes to a faster rate of metalization with applied compressive strain. It arises from the fact that the edge of the conduction band (xz and yz orbital) moves down upon application of compressive strain. Since the optical gap turns out to be between the a_{1g} occupied orbital and the xz and yz unoccupied orbital in agreement with experiments [18] and earlier theoretical works [19].

2.4   Optical Conductivity

We have also computed the optical conductivity of VO_2 in both the rutile and the M1 phase. As shown in Fig. 9, the results are in good agreement with existing experiments. We notice that the value of U that was chosen, not only reproduces the optical gap in the M1 phase but also the value of the quasiparticle renormalization amplitude Z factor in the rutile phase, estimated from
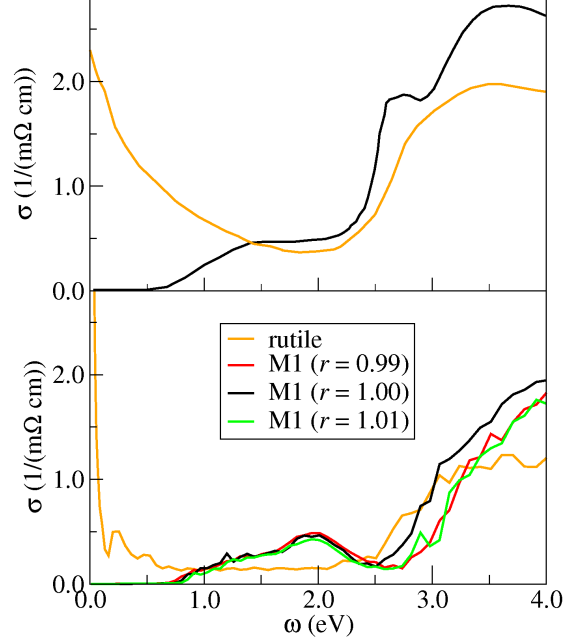
Figure 9: Upper panel: Experimental optical conductivity above and below the MIT measured by [10]. Lower panel: The theoretical optical conductivity in both rutile and M1 phase. The strain in M1 phase leads to increase/decrease of the optical gap.

the weight of the Drude peak. Namely, the ratio of the experimentally measured Drude peak weight, and its estimation from band structure methods is roughly equal to the quasiparticle renormalization amplitude Z. For VO$_2$, the experimental determined weight is $\omega_p^{exp} = 2.75$ eV [13], and the band structure value is $\omega_p^{LDA} \approx 4.1$ eV (obtained by FP-LAPW method [29]) giving the ratio $Z = \omega_p^{exp}/\omega_p^{LDA} \approx 0.67$, which is in very favorable agreement with our DMFT results in rutile phase.

2.4.1 ARPES in the M1 phase

Fig. 10 shows the momentum resolved spectra in the M1-phase. Notice the downshift of the two bonding bands, primarily of $x^2 - y^2$ character (notice that there are four V atoms per unit cell, and hence two bonding $x^2 - y^2$ bands). The states above the Fermi level move slightly up and shrink due to many-body renormalization. They also acquire substantial lifetime around 1 eV. The oxygen bands below -1.5 eV and the eg bands above 2 eV are almost unchanged compared to LDA.

From the theoretical studies, the rutile phase is less sensitive to strain than the M1 phase. The fact that the gap in the density of states arises between
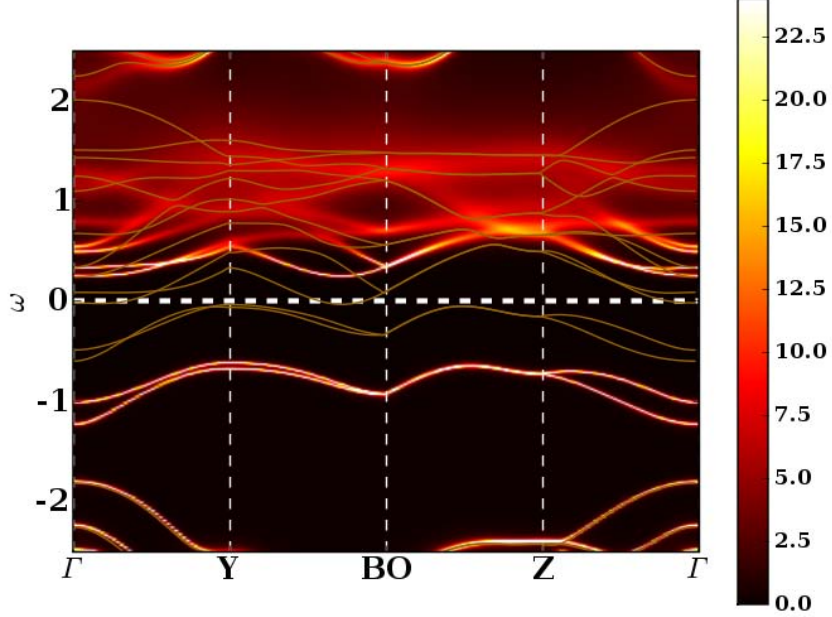
Figure 10: The momentum resolved spectral function $A(\mathbf{k}, \omega)$ along the high symmetry path. The full lines show the LDA bands, and the color-coding shows the LDA+DMFT spectra.

orbitals of different symmetry, indicates that the anisotropy of the transport properties in this phase will be very sensitive to disorder and grain boundaries which can drastically alter the orientation of these orbitals changing the matrix elements for hopping conductivity.

3 Summary

Our exploratory theoretical research set up the machinery for describing the subtle interplay of Coulomb correlations, orbital degeneracy and strain in determining the mechanism of the MIT in VO$_2$. Our theory, coupled with existing strain experiments, clearly show that the Peierls distortion is only one element affecting the MIT and the switching mechanism of this material. The LDA+DMFT calculations in the unstrained material are in good agreement with experiments. We performed the first LDA+DMFT studies of the electronic structure of VO$_2$ under strain. Besides the increase in a_{1g} bonding-antibonding splitting, the low-

ering in energy of the e_g^π orbital, and the rapid change in bandwidth of the a_{1g} orbital, play an equally important role in controlling the position of the MIT. These theoretical insights can be used for understanding and improving material properties by means of chemical substitutions. A paper with these results will be submitted to Physical Review B in the next few weeks. We will continue a more accurate description of the oxygen degrees of freedom, and calculations of the total energy along the transition paths suggested by this exploratory work, to understand in more detail the switching between the two phases, and elucidate the effects of other factors such as the effects of doping on the MIT.

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The change of the VO_2 electronic structure due to application of strain

The V atoms in the insulating M1 phase are dimerized. The Pierls bonds become stronger after compressive strain.

If insulating state is due to Pierls dimerization, the stronger bonds under compressive strain ($c/c_0<1$) would favor insulator, and Tc would increase under compressive strain. Conversely, Tc would decrease when $c/c_0>1$.
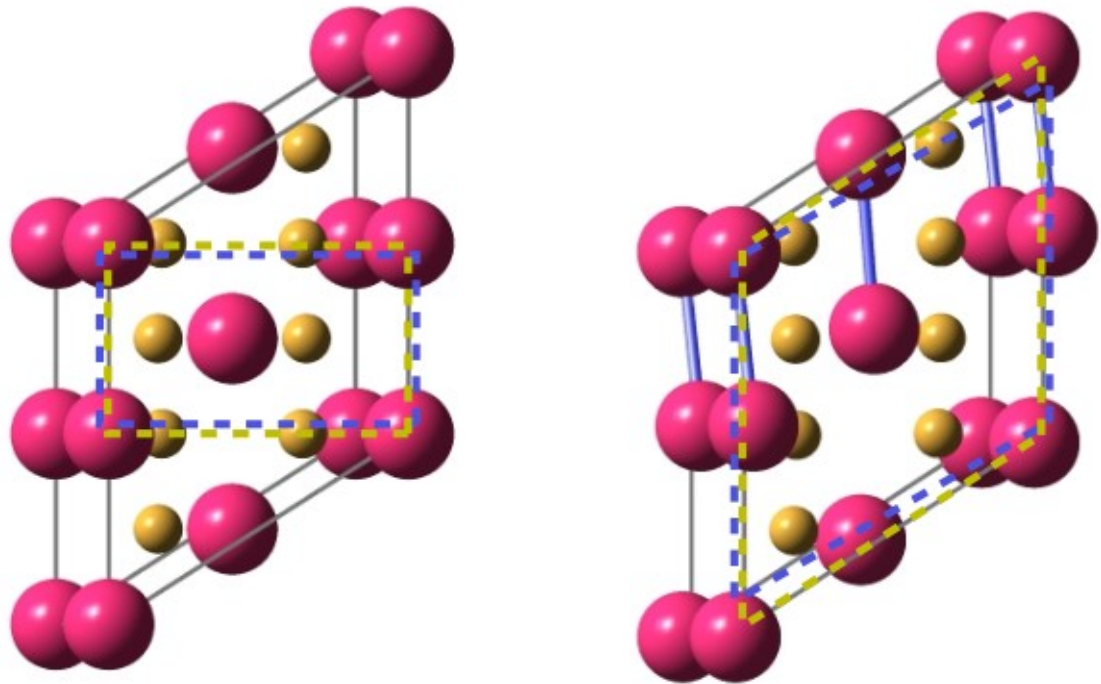
Left: The high temperature metallic rutile structure.
Right: The low temperature insulation M1 structure.

The yellow box shows the unit cell, and the blue box shows the stressed unit cell.

The stress preserves the volume of the unit cell, while it expands (compresses) the rutile c axis and compresses (expands) the rutile a axis.
The actual stress in theory and experiments is 5 x times smaller than shown in the figure.

Dependence of Tc on stress in rutile c axis

Measurements of VO2 tin films on TiO2 substrate show the unexpected result:

Compression of the rutile c axis (achieved on TiO2 (001) substrate) leads to destabilization of insulator, hence Tc decreases.

The expansion of the rutile c axis leads to higher Tc.
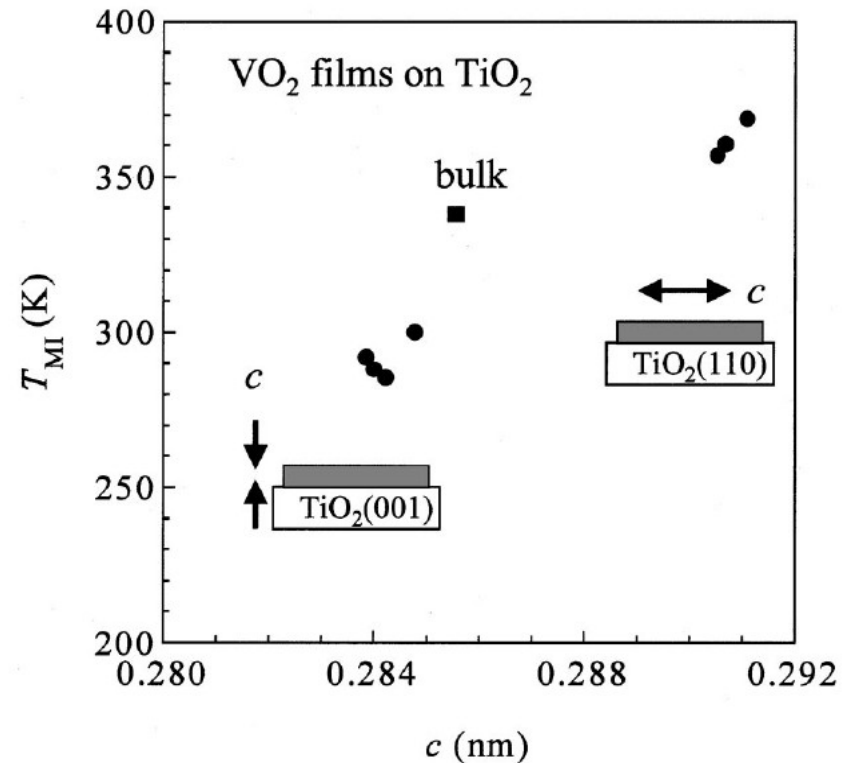
Y. Muraoka and Z. Hiroi, App. Phys. Lett. 80, 583 (2002).

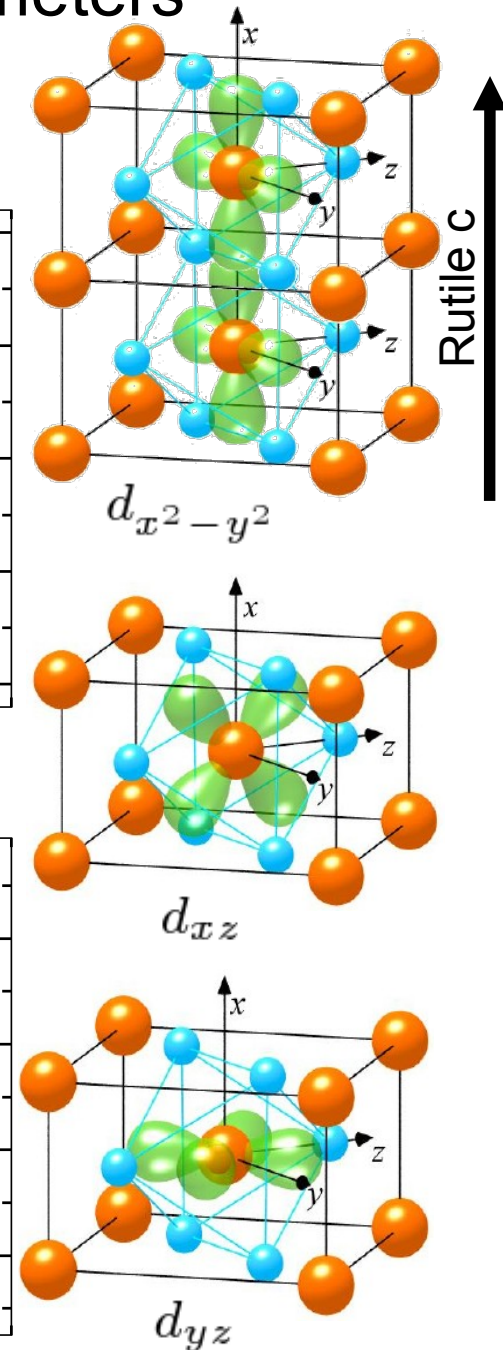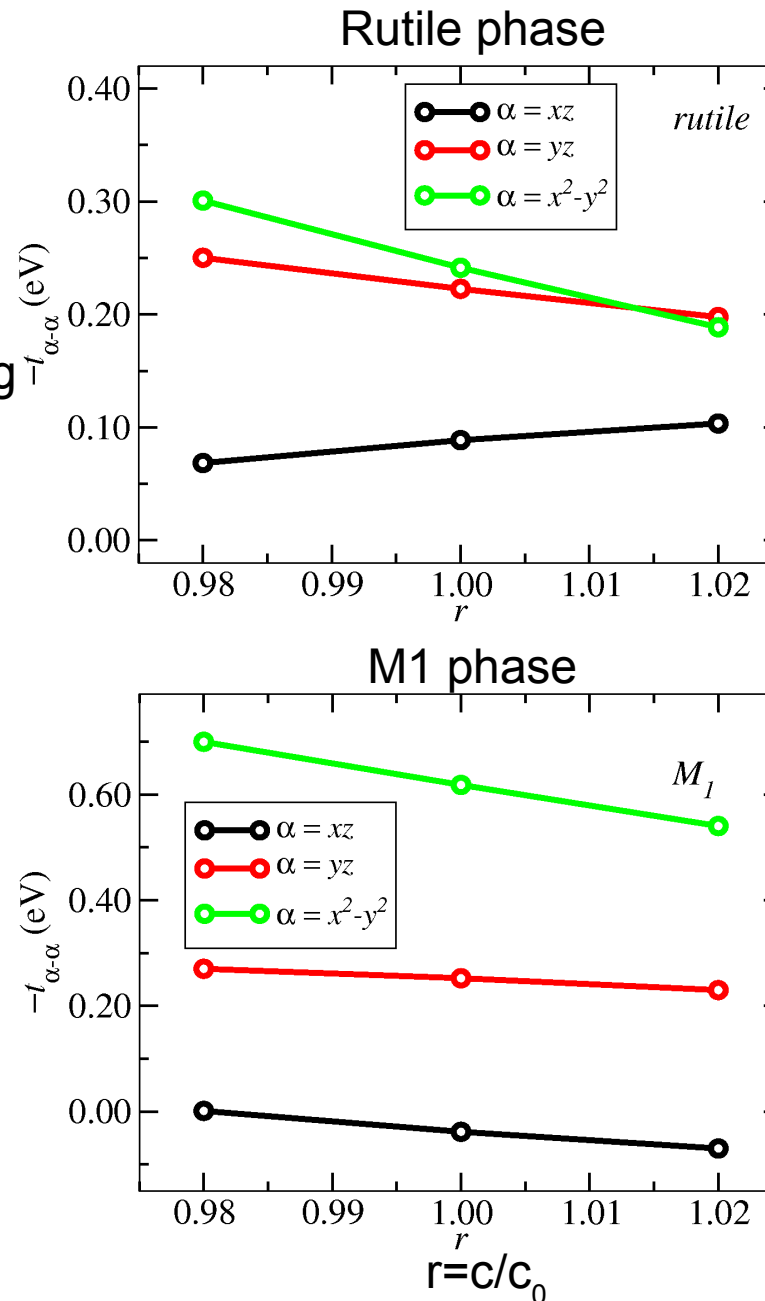# The most important V(3d)-V(3d) hopping parameters within band structure (LDA) calculations

The largest hopping is along the rutile c-axis through x^2-y^2 orbital (upper figure on the right).

In M1 phase the x^2-y^2 hopping (along the Pierls singlet) is twice larger.

The x^2-y^2 hopping increases strongly with compressive stress in rutile c direction in both M1 and rutile phase.
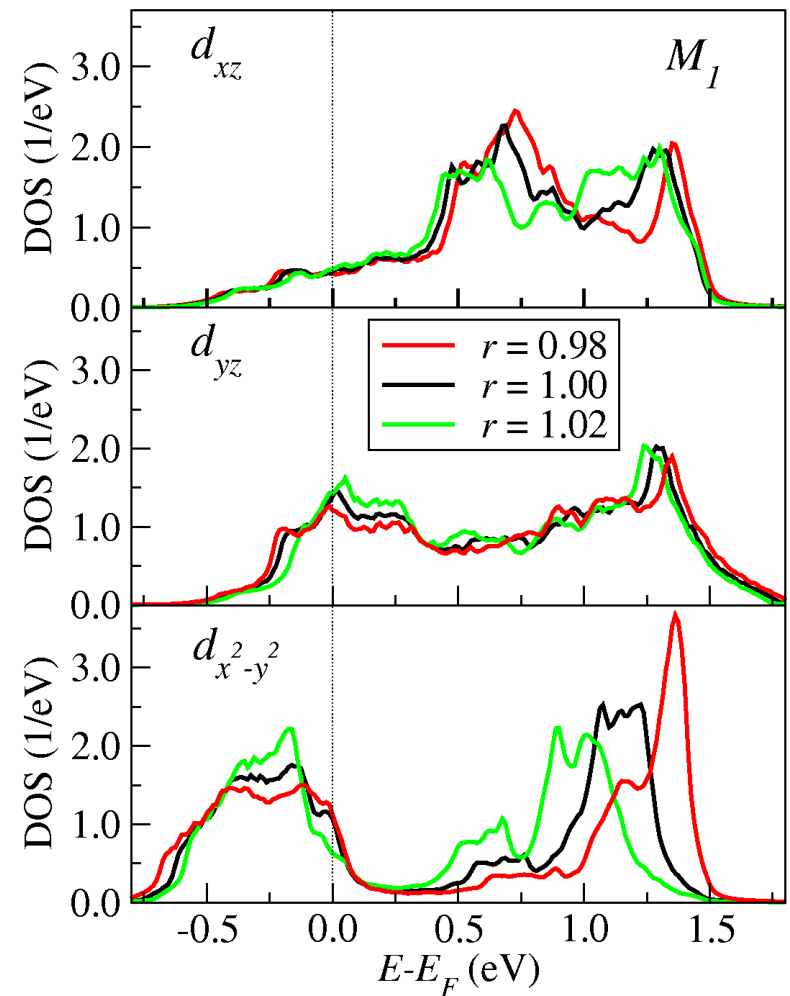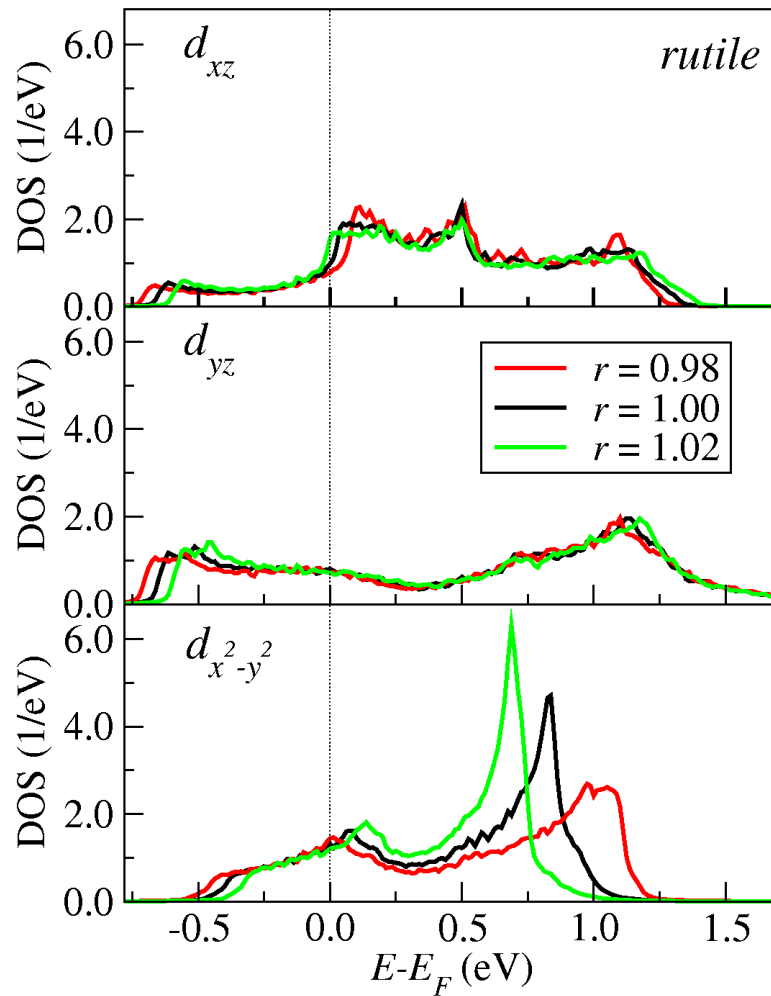
Out of three t_{2g} direct hoppings the magnitude of the small xz hopping decreases with strain, while the other two increase.

Very strong Pierls effect in LDA.

Rutile phase

Legend:
- $\alpha = xz$
- $\alpha = yz$
- $\alpha = x^2-y^2$

rutile

$-t_{\alpha-\alpha}$ (eV)

r

M1 phase

Legend:
- $\alpha = xz$
- $\alpha = yz$
- $\alpha = x^2-y^2$

M_1

$-t_{\alpha-\alpha}$ (eV)

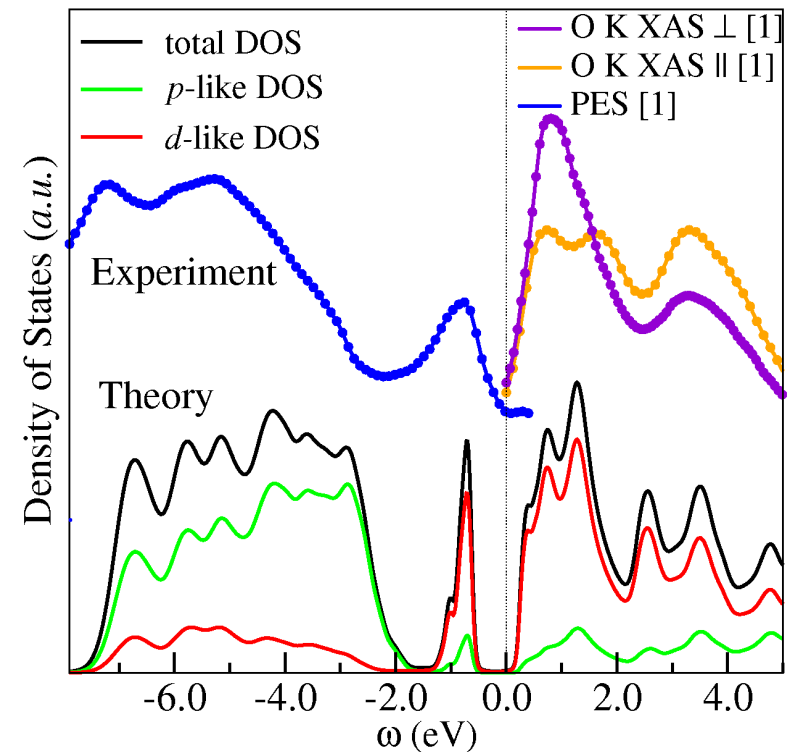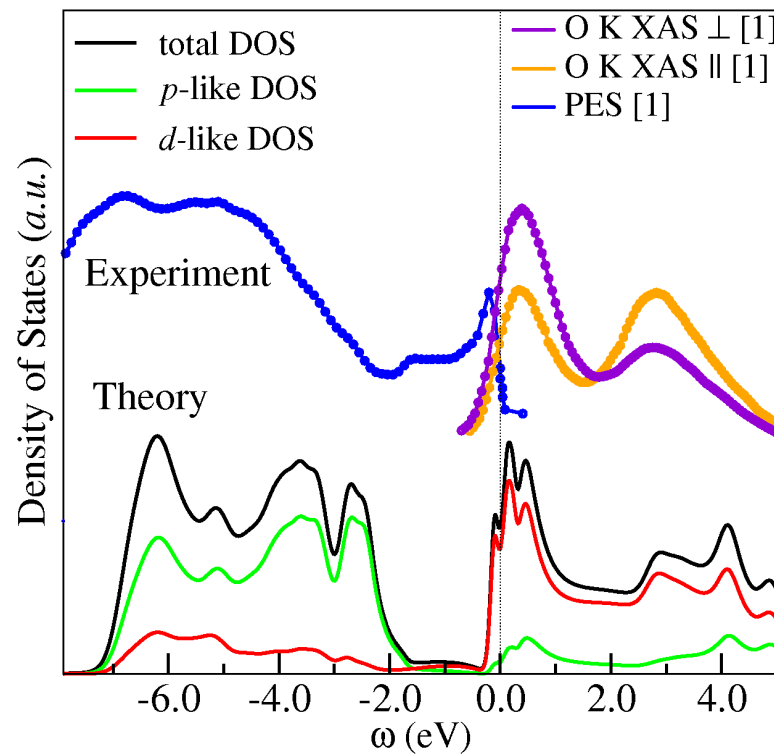r

r=c/c$_0$

Rutile c

$d_{x^2-y^2}$

d_{xz}

d_{yz}

Effects of strain on LDA low energy 3d Density of states

Most of action in x²-y² orbital.
The bonding antibonding splitting increases with compressive strain.

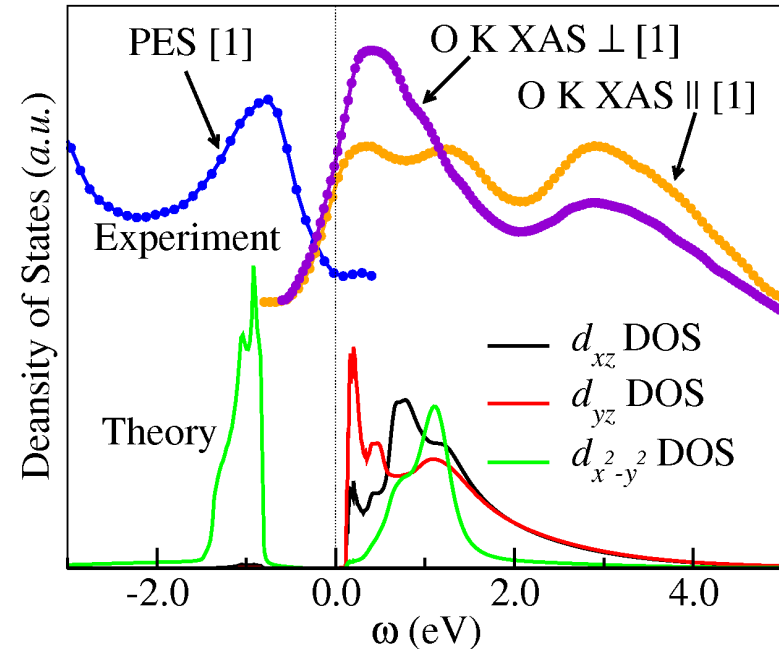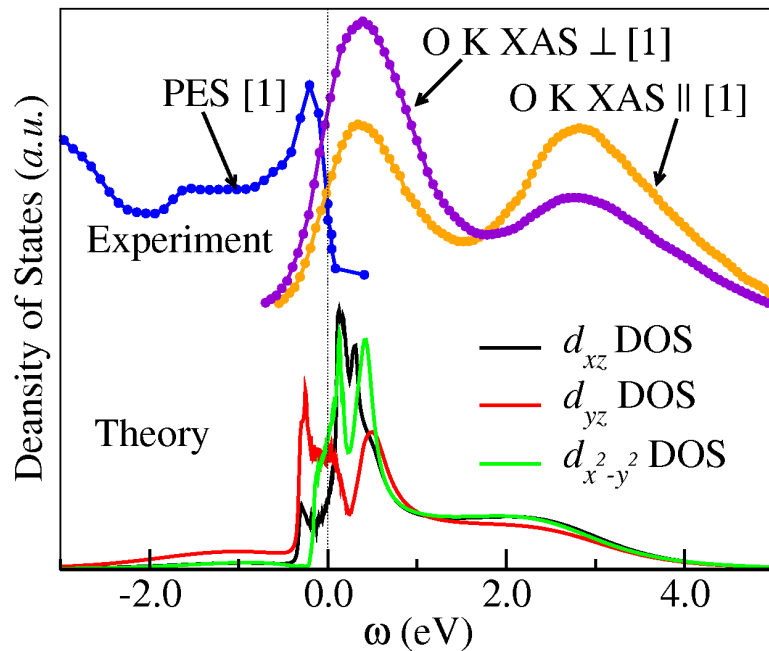# Dynamical Mean Field Theory (DMFT) method for VO$_2$

The rutile 3d-states are substantially narrowed compared to LDA bands.

The M1 phase has a gap of the order of 0.6eV (the screened Coulomb repulsion on the 3d orbital is taken to be 2.2eV in both phases).

The comparison of the DMFT calculations to the PES experiments and O K XAS experiments of Ref.[1] are very encouraging.

[1] T. C. Koethe et al. Transfer of Spectral Weight and Symmetry across the Metal-Insulator Transition in VO2, Physical Review Letters (2006) vol. 97 pp. 116402

# Orbitally resolved V-3d t2g density of states in DMFT

In metallic rutile state, all three t2g's are partially occupied

In the M1 phase, the Mott correlations substantially increase the bonding antibonding splitting of x^2-y^2 orbital to open the gap at the Fermi level. The band gap is not direct gap in the x^2-y^2 orbital. Rather the yz and xz orbitals constitute the conduction band.

Through the presentation, the temperature in the M1 phase is 390K and in the rutile phase is 232K.

The effects of strain on orbitally resolved DOS
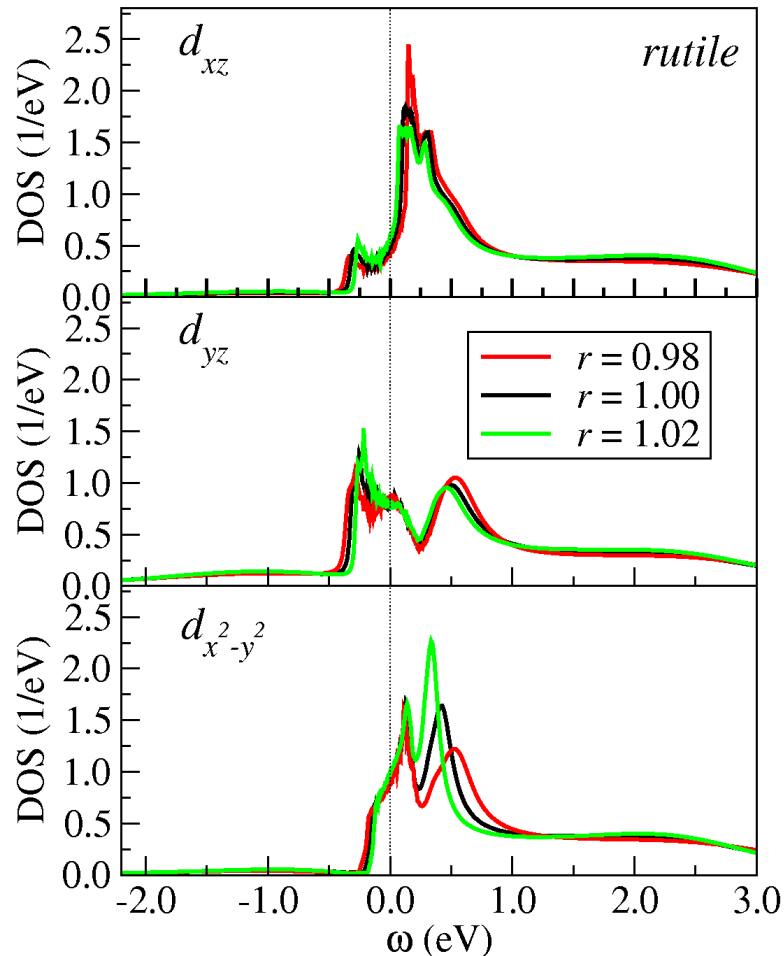
The rutile phase is not much effected by strain, except for slight broadening of the bands with compressive strain
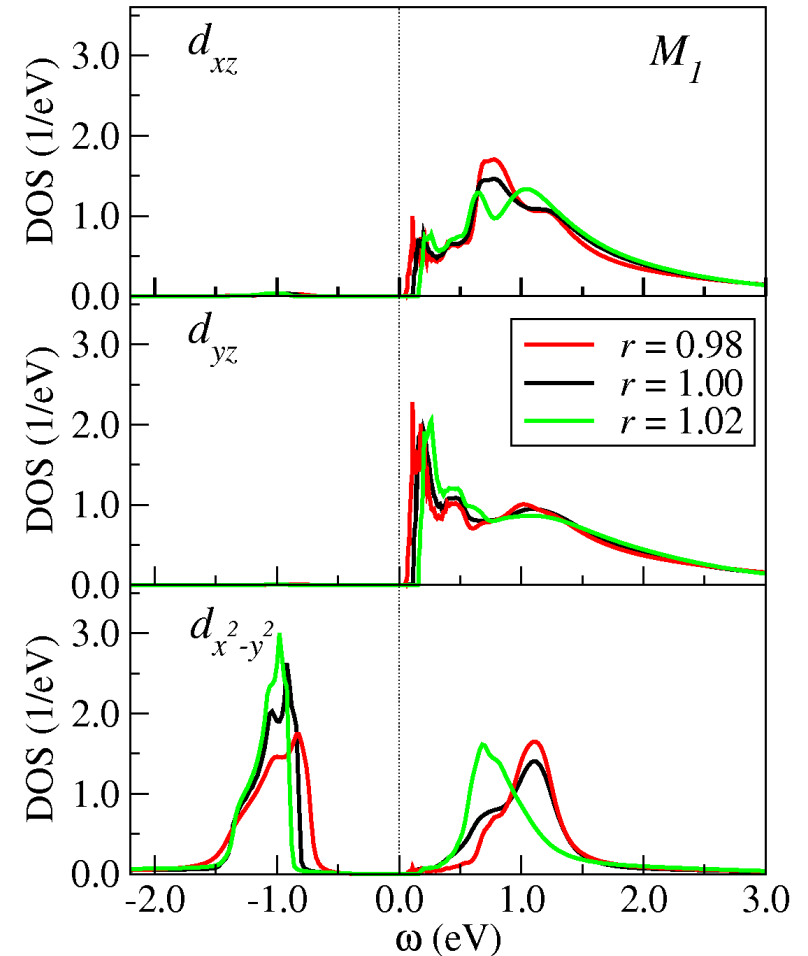
In the M1 phase, the boding-antibonding splitting slightly increases with compressive strain. But the band broadening pushes the system further away from the correlated Mott state. Hence the gap in the x²-y² band slightly decreases.

More importantly, the valence bands of yz and xz orbital move down to decrease the insulating gap.

# The size of the gap in the M1 phase versus strain
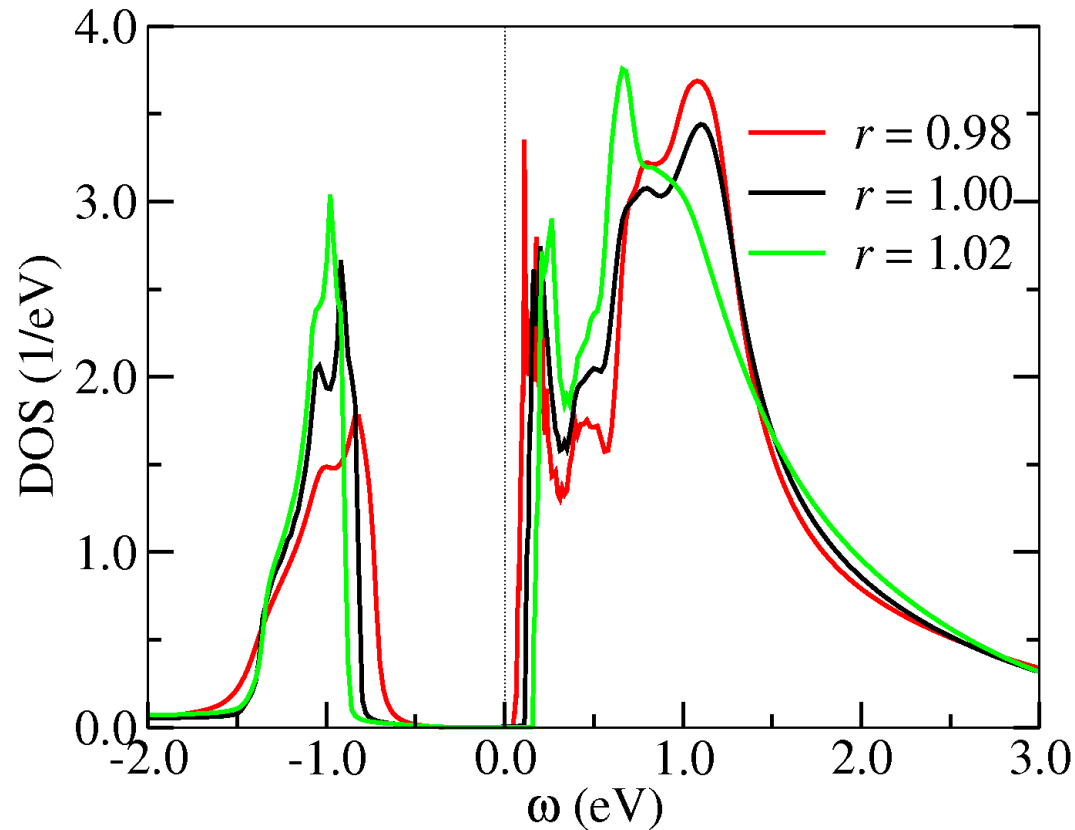
The gap in the M1 phase clearly decreases with compressive strain, contrary to the naive expectations of stronger Pierls bonding-antibonding splitting. This is mainly because of the band broadening effect, which decrease correlation strength, and hence decrease the band gap.

 The second effect contributing to faster metalization with compressive strain comes from the fact that the edge of the conduction band (xz and yz orbital) moves down upon application of compressive strain.

Optical conductivity & strain

Optical gap in the M1 phase increases
with compressive strain.
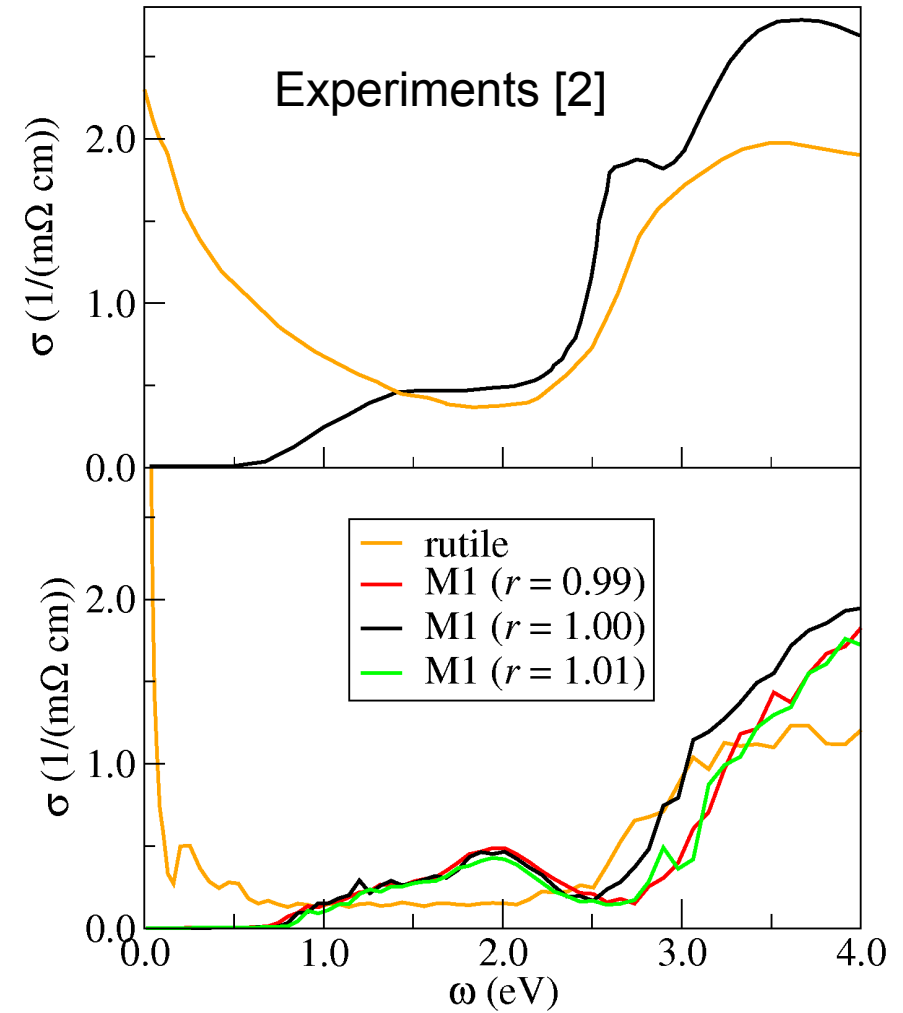
[2] M. M. Qazilbash et al. Correlated metallic state of vanadium dioxide.
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